Critical Grain Size for Microcracking During Lithium Insertion

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Abstract

I derived a critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or grain size is not a practical solution for solving the mechanical instability problem of Li-alloys.

Contents

1. Introduction

The use of Li-alloys (e.g., Li_xM, where M = Al, Bi, Sn, Si, and Ga) as anodes in Li batteries leads to improved safety and faster cycling rates compared to pure Li [1–5]. A disadvantage of Li-alloys compared to pure Li as anodes is a reduction in specific energy and energy density. Another problem with Li-alloy electrodes is mechanical instability. Mechanical instability refers to the microcracking/crumbling of the alloy when Li is inserted/removed during charging/discharging. Some potential solutions to solve the mechanical instability problem include [6–9] (i) incorporating the alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) decreasing the alloy particle and/or grain size. A decrease in the particle and/or grain size is also important from an electrochemical viewpoint, as it can lead to faster cycling rates [10]. However, many questions remain, and among them are these two: How small a grain size is required for the Li-alloys to exhibit mechanical stability during lithium charging/discharging? Are grain sizes of Li-alloy particles produced using new nanophase (particle sizes between 10 to 100 nm) techniques small enough?

This technical note attempts to answer the above questions by determining a critical grain size below which microcracking and, hence, disintegration of the Li-alloy anodes does not occur during Li charging.

2. Discussion

Microcracking occurs in Li-alloys as a result of volume expansion during Li charging. The determination of the critical grain size below which microcracking does not occur is based on an energy criterion. The basic concept of the energy criterion is that the strain energy (generated due to a volume difference between phases) released when microcracks form must equal or exceed that required for the creation of new fracture surfaces. The energy criterion has been successfully applied to explain crack formation in brittle materials, microcracking due to thermal shock, and thermal expansion anisotropy [11–13].

We can start with a single particle composed of fine equiaxed grains. The total energy of this system, U_{tot}, is given as follows [11–13]:

$$U_{tot} = U_0 - U_{strain} + U_{surface} , \qquad (1)$$

where U_0 is the energy of the unmicrocracked particle, U_{strain} is the strain energy per unit volume, and $U_{surface}$ is the surface energy per unit area. The following discussion assumes that microcracking (i) is due to tensile stresses generated as a result of volume expansion and (ii) occurs along grain boundaries. Assuming a dodecahedral grain morphology of grain size, d, equation (1) reduces to [13]

$$U_{tot} = U_0 - 7.66 \, N U_{strain} \, d^3 + 20.65 \, N\gamma d^2 , \qquad (2)$$

where N is the number of grains that relieve their elastic strain energy by microcracking and γ is the surface energy. The critical grain size, d_{crit}, is calculated by differentiating equation (2) and equating it to zero as follows:

$$d_{crit} = 1.79 \; \gamma / U_{strain} \; . \tag{3}$$

The importance of equation (3) is that a material with a grain size smaller than d_{crit} will not exhibit microcracking; whereas if the grain size is greater than d_{crit}, it will exhibit microcracking. Assuming only elastic behavior, the strain energy is given as follows:

$$U_{strain} = \sigma^2 / 2E \; , \tag{4}$$

where σ is the stress and E is the elastic modulus. For the case of a volume change, the stress is given as follows [14]:

$$\sigma = \frac{E}{3(1-2\nu)} \frac{\Delta V}{V_0} \; , \tag{5}$$

where ΔV is the volume change, V_0 is the initial volume, and ν is Poisson's ratio. Substituting equation (5) into equation (4) and combining it with equation (3) yields the following equation for the critical grain size as a function of volume change:

$$d_{crit} = \frac{32.2\gamma(1-2\nu)^2 V_0^2}{E \Delta V^2} \; . \tag{6}$$

Equation (6) can be used to determine how small a grain size is required for Li-alloys (e.g., $Li_x M$, where M = Al, Bi, Sn, Si, and Ga) that are used as anodes and that do not exhibit microcracking during lithium charging. A material with a grain size less than d_{crit} (eq. (6)) will not exhibit microcracking as a result of tensile stresses generated due to a volume expansion.

What is the critical grain size of an Li-alloy that is to be used as an anode in Li batteries? For example, take $Li_{4.4}Sn$. This binary alloy has the highest Li capacity in the Li-Sn system [7]. The volume change, $\Delta V / V_0$, from Sn to $Li_{4.4}Sn$ is 2.59 per atom of Sn [7,15]. Determination of the critical grain size also requires that E, ν, and γ be known. Unfortunately, a review of the literature did not reveal the values of E, ν, and γ for $Li_{4.4}Sn$. The average E for 20 other intermetallic alloys is close to 200 GPa [16]. The surface energy for brittle materials is typically between 0.3 to 1.2 J/m^2 [17]. Using E = 200 GPa, γ = 0.75 J/m^2, ν = 0.33 (a typical value for a crystalline solid), and $\Delta V / V_0$ = 2.59, the critical grain size below which microcracking will not occur during Li charging of Sn to $Li_{4.4}Sn$ can be determined. Inserting these values into equation (6) yields a predicted $d_{crit} \approx 0.002$ nm. If the value of the surface energy is off by a factor of 2, and the elastic modulus is off by a factor of 10, the predicted critical grain size is still less than 0.040 nm. It is important to note that this grain size (0.040 nm) is about 12 to 13 times smaller than the size of an Sn unit cell (≈ 0.5 nm). A similar

calculation for $Li_{4.4}Si$ ($\Delta V / V_0 = 3.12$ [7]) yields a predicted $d_{crit} \approx$ 0.0014 nm. These results suggest that it is almost impossible to obtain a fine enough grain size to prevent microcracking during Li charging of a single-phase material. It is believed that this is primarily a result of the strain energy generated by large tensile stresses due to the volume change that cannot be accommodated by plastic deformation due to the brittle nature (significant fraction of covalent or ionic bonding) of the material and, hence, microcracking occurs. The above predictions are in agreement with experimental electrochemical results, which reveal that it is almost impossible to electrochemically insert Li into fine grain pure metals such as Sn to form Li-Sn alloys without the alloys suffering cracking/ disintegration [15,18]. Even if a sacrifice in capacity is made to reduce the amount of volume expansion, the predicted critical grain size is still less than the size of a unit cell for most of the Li-alloys. For example, Li charging of Sn to form LiSn ($\Delta V / V_0 = 0.53$) instead of $Li_{4.4}Sn$ only increases the critical grain size by a factor of about 25, to about 0.05 nm. This grain size is still much smaller than the size of the Sn unit cell. The above predictions and their agreement with the experimental observations emphasize that producing a fine enough grain size in an intrinsically brittle single-phase material to prevent microcracking as a result of a volume expansion due to Li charging is highly unlikely, no matter what processing technique is used, including new nanophase techniques.

The results suggest that decreasing the particle and the grain size is not a practical solution to solve the mechanical instability problem of Li-alloys. More likely solutions to solve this problem include (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix as previously suggested [6–9] or (ii) surrounding the alloys within a matrix that places them under compressive stresses to prevent microcracking formation. This suggestion may explain why SnO and SnO_2 can be cycled, whereas metallic Sn cannot [15,18,19]. It has been observed that as Li is initially titrated into SnO or SnO_2, it decomposes to Li_2O and Sn. Upon further Li addition, a series of Li-Sn alloys form with increasing Li content until a final alloy composition of $Li_{4.4}Sn$ is reached [15,19,20]. It is likely that the Li_2O surrounding the Li-Sn alloys supplies a residual compressive stress that prevents the Li-Sn alloys from suffering mechanical deterioration during repeated charging/discharging. This same reasoning may also explain why $Li_2MnO_4 / Na_{0.7}MnO_2$ composites exhibit better capacity retention during cycling in the 3-V region compared to single-phase Li_2MnO_4 [21].

3. Conclusions

A critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys was derived based on energy considerations. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or the grain size is not a practical solution for solving the mechanical instability problem associated

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with Li-alloys. More likely solutions to this problem include (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) surrounding the alloys within a matrix that places them under a compressive stress.

Acknowledgments

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